

JAPANESE

[JP,08-239528,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL
FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention about the multilayer-structure object which extends an ethylene-vinylacetate copolymer saponification thing (it omits the following EVOH), the resin composition containing specific polyamide system resin, and this resin composition, The voile sterilization excellent in the retort-proof nature which used the EVOH system resin composition and this resin which were excellent in long-run shaping or ductility in detail, or voile-proof nature or the multilayer film wrapping material for retort sterilization processing, It is related with multilayer-structure objects, such as a container for retort sterilization processing, a gas tank excellent in the lid material for retort sterilization processing, or damping

nature, and a structural interior material.

[0002]

[Description of the Prior Art]The constituent of EVOH and polyamide system resin is used for various uses, such as a film, a sheet, parison, a container, a gas tank, etc. for food packing, using the gas barrier property, oil resistance and solvent resistance based on the former, and the shock resistance based on the latter. And as a constituent of EVOH and polyamide system resin which are used for this use, the constituent (JP,54-78749,A.) of the conventional EVOH and polyamide system resin For the purpose of improvement of the moldability of JP,54-78750,A, JP,62-225535,A, JP,4-76040,A, and JP,4-178447,A, these people, It proposed blending a hindered phenol system compound and aliphatic-carboxylic-acid alkaline earth metal salt with the mixed material of EVOH and specific end preparation polyamide system resin further. (Japanese Patent Application No. No. 164013 [five to])

On the other hand, polyamide system resin is blended with two sorts of EVOH(s) (JP,63-56893,B, JP,4-202549,A), and improvement in ductility or a long-run moldability is tried. Using for the door mirror stay (JP,1-263151,A) of a car, etc. the resin composition which consists of EVOH and polyamide system resin as the hose for refrigerant gases (JP,2-86436,A) to which load of the vibration is carried out continuously, or a sound deadener use is proposed.

[0003]

[Problem(s) to be Solved by the Invention]however, in the Japanese-Patent-Application-No. No. 164012 [five to] indication art by these people, in the use of draw magnification with an area magnification of about 3 to 10 times, although it can fully be equal to practical use, in the commercial scene of these days, the Takanobu extensibility with an area magnification of 20 or more times is demanded, and the necessity for a new improvement has arisen. In JP,63-56893,B indication art. A moldability for ductility (however, 200% extension) to obtain the film before extension of a good thing, When it was not taken into consideration in particular about a long-run moldability, but long-run shaping of the 5th day or more was performed according to this invention person's etc. examination, it became clear that there was fear of generating of gel, a fish eye, a film piece, regurgitation instability (surging

phenomenon), etc. Although JP,4-202549,A indication art was made that this point should be improved, about the Takanobu extensibility, there is room of improvement still more like the Japanese-Patent-Application-No. No. 164012 [five to] indication art.

[0004]In JP,2-86436,A indication art. Although pinhole-proof nature, crack resistance, etc. about a hose which consist of a constituent of EVOH and polyamide system resin are taken into consideration, about the moldability of this constituent, or ductility. It is not taken into consideration at all, but JP,1-263151,A indication art, It is a thing about molding (engineering plastics), such as a door mirror stay of a car, There is no consideration of gas barrier property peculiar to EVOH etc., and also it is taken into consideration at all about neither the moldability of this constituent, nor ductility as well as JP,2-86436,A indication art, and there is room of improvement still more. An object of this invention is to provide the multilayer-structure objects the object for retorts, for sound deadeners, etc. using an EVOH system resin composition and this resin outstanding under such a background at a long-run moldability, the Takanobu extensibility with an area magnification of 20 or more times, etc.

[0005]

[Means for Solving the Problem]As a result of this invention person's etc. examining this technical problem wholeheartedly, ethylene content at 20-60-mol % An ethylene-vinylacetate copolymer saponification thing of not less than 95% of the degree of saponification (a), In ethylene content, the degree of saponification at 25-65-mol % An ethylene-vinylacetate copolymer saponification thing beyond 70 mol % (b), Make KAPURO amide into a main constitutional unit, and a ratio of the number of methylene groups to the number of amide groups by aliphatic polyamide which satisfies $5.20 \leq \text{CH}_2/\text{NHCO} \leq 6.50$.

Terminal carboxyl group content [X] and terminal amino group content [Y] using an end regulator And $[Y] < [X] + 5$. (however, a unit of [X] and [Y] consisting of end adjustment polyamide system resin (c) and aliphatic-carboxylic-acid alkaline earth metal salt (d) which were adjusted so that mueq/g and polymer) might be satisfied, and, ethylene content of (b) -- ethylene content of (a) -- more than 3 mol % -- and a weight ratio of (a): (b) by 90:10 to 10:90. By

50:50-96:4, an EVOH system resin composition whose blending ratio of (d) is 0.5-15 micro mol/g in metal conversion Gas barrier property, oil resistance, [as opposed to the total quantity of (a+b+c) in a weight ratio of (a+b): (c)] Without reducing the characteristic which EVOH(s), such as solvent resistance, have A long-run moldability, Excel in the Takanobu extensibility with an area magnification of 20 or more times etc., and especially Voile sterilization or retort sterilization. (Retort sterilization is called collectively hereafter) A useful thing was found out on multilayer-structure objects for which a film package material for processing and damping nature are needed, such as a gas tank, a structural interior material, and a hose for refrigerant gases, and it resulted in completion of this invention.

[0006]

[Embodiment of the Invention] Hereafter, this invention is explained in detail. As EVOH (a) of this invention, the thing beyond 95 mol % (preferably 98-mol % more than) is used for the degree of saponification of a vinyl acetate unit the ethylene content 20 - 60-mol% (preferably 25-55-mol %). If ethylene content causes the fall of melt molding nature less than [20 mol %] and ethylene content exceeds 60-mol % conversely, the fall of oxygen gas barrier property will be caused, hot water resistance is inferior in the degree of saponification, and it is unsuitable less than [95 mol %]. if this EVOH (a) comes out in small quantities and there is, even if "copolymerization denaturation" is carried out by other comonomers, such as alpha olefin, an unsaturated-carboxylic-acid system compound, an unsaturation sulfonic acid system compound, acrylonitrile (meta-), acrylamide (meta-), vinyl ether, VCM/PVC, and styrene, it will not interfere. In the range which does not spoil the meaning of this invention, even if it acetalizes [urethane-ization,] and cyanoethylates "post-denaturation", it does not interfere.

[0007] As for above EVOH (a) and EVOH (b) used together, the thing beyond 70 mol % (preferably 80-mol % more than, still more preferably 85-mol % more than) is used for the degree of saponification of a vinyl acetate unit the ethylene content 25 - 65-mol% (preferably 30-60-mol %). About ethylene content and the degree of saponification, it is specified in the above-mentioned range for a reason equivalent to EVOH (a), and even if "it denaturalizes

[back]", it does not interfere. [same / "the copolymerization denaturalizing" / as the above-mentioned EVOH (a) or] In this invention, the ethylene content of EVOH (b) rather than the ethylene content of EVOH (a) However, more than 3 mol %. desirable -- more than 5 mol % -- it is necessary to make [many] it, the Takanobu growth with an area magnification of 20 or more times becomes the improvement effect of the ductility [difference / of this content] in less than [3 mol %] is not enough, and impossible, and it is unsuitable. the time of expecting the further ductile improvement, although not limited in particular for the difference of the degree of saponification -- the degree of saponification of EVOH (a) -- the degree of saponification of EVOH (b) -- more than 1 mol % -- a large thing is preferred.

[0008]As end adjustment polyamide system resin (c), KAPURO amide is made into a main constitutional unit, and the ratio of the number of methylene groups to the number of amide groups is the aliphatic polyamide which satisfies $5.20 \leq \text{CH}_2/\text{NHCO} \leq 6.50$, And the polyamide system resin adjusted so that terminal carboxyl group content [X] and terminal amino group content [Y] might satisfy $[Y] < [X] + 5$ (however, [X] and the unit of [Y] mueq/g and polymer) using an end regulator is used.

[0009]In order to obtain such end adjustment polyamide system resin (c), copolymerization of other aliphatic polyamide is first carried out to a KAPURO amide ingredient. Especially the Capurro amide unit in this copolymer 95 to 55% of the weight 90 to 60 % of the weight, When it is desirable for 90 to 65 % of the weight to exist above all and there are too much few Capurro amide units, the modification effects of EVOH (a+b) run short, When there are too much many Capurro amide units, the temperature at the time of melt molding when it mixed and uses for EVOH (a+b) becomes high, and is subtracted at long-run shaping. As other aliphatic polyamide which carries out copolymerization to a KAPURO amide ingredient, the aminocarboxylic acid of the carbon numbers 6-12, lactam and dibasicity acid of the carbon numbers 6-12, diamine of the carbon numbers 4-10, etc. are raised.

[0010]The amide group concentration of the above-mentioned copolymer requires that the ratio of the number of methylene groups to the number of amide groups should

be within the limits of $5.20 \leq \text{CH}_2/\text{NHCO} \leq 6.50$. the more desirable range -- 5.20-6.00 -- it is 5.30-5.80 especially. For that purpose, it is required for amide group concentration to introduce ten or more ingredients 10% of the weight or more preferably 5% of the weight or more into a whole copolymer. When the ratio of the number of methylene groups to the number of amide groups is smaller than a mentioned range, a long-run moldability is spoiled, when more than a mentioned range, the Capurro amide units in a copolymer run short, and the modification effects of EVOH (a+b) run short.

[0011]As an example of the above-mentioned copolymer, the copolymer which serves as nylon 6 from Nylon 66, Nylon 11, Nylon 12, Nylon 610, etc. is raised, and copolymers, such as Nylon 612, nylon 6 and 11, the nylon 6 66 and 12, and the nylon 6 66 and 11, are preferred especially. As for especially the melting point of a copolymer, it is desirable for there to be 160-215 °C within the limits of 165-215 °C.

[0012]Although the above-mentioned copolymer has a carboxyl group and an amino group, it is required that this terminal carboxyl group content [X] and terminal amino group content [Y] should satisfy $[Y] < [X] + 5$ (however, [X] and the unit of [Y] meq/g and polymer). That is, it must be adjusted so that the content of the terminal carboxyl group in a molecule may become larger than the content of a terminal amino group by an end modifier. In this case, as for the absolute value of terminal amino group content [Y], it is [below 70 meq/g and polymer] desirable that it is below 50 meq/g and polymer especially. There is terminal amino group content [Y] that it is disadvantageous in respect of a long-run moldability, when large. on the other hand, there is little terminal amino group content [Y] -- this -- better -- since manufacture of resin becomes difficult, °C should limit to 10 meq/g and a polymer grade. It is [below 100 meq/g and polymer] appropriate for the absolute value of terminal carboxyl group content [X] that below 70 meq/g and polymer carry out especially.

[0013]As an end modifier in the above, the carboxylic acid of the carbon numbers 2-23 and diamine of the carbon numbers 2-20 are used. Here as monocarboxylic acid of the carbon numbers 2-23, aliphatic monocarboxylic acid (acetic acid, propionic acid, butanoic acid, a valeric acid, and

caproic acid.) Enanthic acid, caprylic acid, capric acid, pelargonic acid, undecanoic acid, Lauryl acid, tridecanoic acid, myristic acid, milli train acid, PAL methine acid, Alicyclic monocarboxylic acid (cyclohexane carboxylic acid, methylcyclohexane carboxylic acid, etc.), such as stearic acid, oleic acid, linolic acid, arachin acid, and behenic acid, aromatic monocarboxylic acids (benzoic acid, torr yne acid, ethylbenzoic acid, phenylacetic acid, etc.), etc. are raised.

[0014]as the diamine of the carbon numbers 2-20 -- aliphatic diamine (ethylenediamine.) Trimethylene diamine, a tetramethylenediamine, pentamethylene diamine, Hexamethylenediamine, octamethylenediamine, decamethylenediamine, Dodecamethylenediamine, hexadecamethylene diamine, 2,2,4-(or 2,4,4-) trimethyl hexamethylenediamine, etc., Alicyclic diamine (a cyclohexanediamine, bis-(4,4'-aminocyclohexyl)methane, etc.), aromatic diamine (xylylene diamine etc.), etc. are mentioned.

[0015]everything but the above-mentioned monocarboxylic acid -- aliphatic dicarboxylic acid (malonic acid.) Succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, Sebacic acid, dodecane dione acid, tetradecanedione acid, hexadecanedione acid, Hexa decene dione acid, octadecanedione acid, octadecene dione acid, Eicosadione acid, eicosen dione acid, docosanedione acid, 2,2,4-trimethyl adipic acid, etc., Dicarboxylic acid, such as alicyclic dicarboxylic acid (1,4-cyclohexanedicarboxylic acid etc.) and aromatic dicarboxylic acid (terephthalic acid, isophthalic acid, phthalic acid, xylylene dicarboxylic acid, etc.), can also be used or used together.

[0016]Although the amount in particular of the end modifier used is not limited, the quantity of a carboxyl group usually uses for 0.2 - 15 overmeq/mol preferably 0.1 to 18 meq/mol rather than the quantity of an amino group. When there is too much little amount of the end modifier used, the improvement effect of a long-run moldability is scarce, and when on the other hand too much large, the rise of a degree of polymerization is slow and is not preferred on manufacture. As for the degree of polymerization of polyamide, although limitation in particular is not carried out, it is preferred 1.7-4.0, and that it is 2.0-4.0 especially at the relative viscosity measured according to JIS K6810.

[0017]As a polymerization method of polyamide, melt polymerization, an interfacial polymerization, solution polymerization, mass polymerization, solid state polymerization, or the method that combined these is employable. Especially epsilon caprolactam is more preferred than the point that better voile-proof nature and retort-proof nature are obtained as a polyamide raw material. As aliphatic-carboxylic-acid alkaline earth metal salt (d), The beryllium salt of with a carbon number of about one to nine aliphatic carboxylic acid, such as acetic acid, propionic acid, butanoic acid, a valeric acid, caproic acid, and Capri acid, Magnesium salt, calcium salt, strontium salt, and barium salt are mentioned, and magnesium salt and calcium salt of aliphatic carboxylic acid of the carbon numbers 2-4 are especially important.

[0018]Although the EVOH system resin composition of this invention consists of EVOH(a) EVOH(b) end adjustment polyamide system resin (c) and aliphatic-carboxylic-acid alkaline earth metal salt (d) like the above, It is required for the blending ratios of (a) and (b) to be 90:10-10:90 in a weight ratio about the blending ratio, It is 80:20-20:80 preferably, and out of a mentioned range, when there are more ductility improvement effects of the last resin composition than the weight ratio which is not enough and are above-mentioned [the blending ratio of (b) / this] the weight ratio, gas barrier property falls. When (a+b) and the blending ratio with (c) need to be 50:50-96:4 at a weight ratio and there are few blending ratios of end adjustment polyamide system resin (c) than this weight ratio, The improvement effect of voile-proof nature and retort-proof nature does not fully show up, and the improvement effect of ductility and damping nature is not enough, and when conversely large, the oxygen gas barrier property which EVOH (a+b) has is spoiled. It is 70:30-90:10 preferably.

[0019]The blending ratio of aliphatic-carboxylic-acid alkaline earth metal salt (d), To the total quantity of (a+b+c), by metal conversion 0.5 - 15micromol/g, It is required to be 1-9micromol/g preferably, and if the rise of melt viscosity is caused and 15micromol/g is exceeded conversely, generating and foaming of gel will be produced at the time of shaping, or coloring of a film and destabilization of a moldability may be caused and it is unsuitable at less than 0.5micromol/g. The EVOH system

resin composition which consists of above-mentioned (a) - (d) can blend suitably additive agents, such as a plasticizer, a filler, an antiblocking agent, colorant, a spray for preventing static electricity, and an ultraviolet ray absorbent, in addition to the above.

[0020]it being effective to blend further a hindered phenol system compound (e) and lubricant (f), and as a hindered phenol system compound (e), in order to acquire especially the further effect of this invention, N,N'-hexa methylenebis (3,5-di-t-butyl-4-hydroxyhydronalium SHINNAMIDO), 1,1,3-tris(2-methyl-4-hydroxy-5-t-buthylphenyl) butane, 1,3,5-trimethyl 2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl) benzene, tetrakis [Methylene-3-(3' and 5'-di-t-butyl-4'-hydroxyphenyl) propionate] n-octadecyl-beta-(4'-hydroxy-3' and 5'-di-t-buthylphenyl) propionate, 2,2'-methylene bis (4-methyl-6-t-butylphenol), 2,2'-methylene bis (4-ethyl-6-t-butylphenol), 4,4'-thiobis (6-t-butyl-m-cresol), 4,4'-thiobis (3-methyl-6-t-butylphenol), pentaerythrityl tetrakis [3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] ***** is mentioned and they are N,N'-hexa methylenebis (3,5-di-t-butyl-4-hydroxyhydronalium SHINNAMIDO), 1,3,5-trimethyl 2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl) benzene, and pentaerythrityl tetrakis preferably. [3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate] ***** -- a kind is used even if small.

[0021]The blending ratio of a hindered phenol system compound (e), When it is preferred that it is in 0.005 to 1 % of the weight of the range to the total quantity with (a+b+c) and there are few blending ratios of a hindered phenol system compound (e) than a mentioned range, Since antioxidizing nature runs short, it does not become that it is easy to produce oxidizing gel and a dice holdup during shaping, or the multilayer-structure object where the synergistic effect with the aliphatic-carboxylic-acid alkaline earth metal salt (d) shown above fell and which was excellent in film appearance is not acquired. On the other hand, even if it makes the blending ratio more than a mentioned range, the depressor effect of high-temperature-oxidation nature gel and the synergistic effect with aliphatic-carboxylic-acid alkaline earth metal salt (d) do not improve beyond a fixed limit, It becomes disadvantageous in cost, is 0.05 to 0.8 % of the weight still more preferably, and is 0.1 to 0.5 % of the weight especially preferably.

[0022]As lubricant (f), ethylene screw fatty acid (carbon numbers 16-18) AMAIDO, such as ethylene screw stearyl AMAIDO, Higher-fatty-acid metal salt, such as higher-fatty-acid (carbon numbers 8-22) AMAIDO, zinc stearate, aluminum stearate, calcium stearate, and magnesium stearate, If the horse mackerel peat system condensate of a polypropylene glycol, the SEBATO system condensate of polypropylene, and polymers ester [, for example, a trade name, are mentioned, If spar MUASECHI (made by Nippon Oil & Fats Co., Ltd.), Hoechst wax E (made by Hoechst Japan), rye toll (made by Sanwa fats-and-oils company), and haze wax (made by Noda wax company)] and fatty-acid-ester [, for example, a trade name, are mentioned, Butyl stearate, the Nissan caster wax A (above, Nippon Oil & Fats Co., Ltd. make). The molecular weight by TB-121(made by Matsumoto Yushi-Seiyaku)] and a viscosity method Low-molecular-weight polyolefines, such as polyethylene of 900-30000, By 1000-20000, in acid value, low-molecular-weight polyolefines, such as modified polyethylene of the range of 5-100 and denaturation polypropylene, etc. are mentioned, and the molecular weight by a viscosity method preferably Ethylene screw fatty acid (carbon numbers 16-18) AMAIDO, such as ethylene screw stearyl AMAIDO, Higher-fatty-acid metal salt, such as higher-fatty-acid (carbon numbers 8-22) AMAIDO, zinc stearate, aluminum stearate, calcium stearate, and magnesium stearate, Low-molecular-weight polyolefines, such as modified polyethylene of the range of 5-100 and denaturation polypropylene, are used [the molecular weight by a viscosity method] for acid value by 1000-20000, and zinc stearate and calcium stearate are used still more preferably.

[0023]Although the blending ratio of lubricant (f) cannot generally be said according to the kind, 0.001 to 1 % of the weight is desirable still more preferred to the total quantity of the above (a+b+c), and it is 0.01 to 1 % of the weight. When this blending ratio causes the increase in the holdup in an extrusion machine or a dice at less than 0.001 % of the weight and exceeds 1 % of the weight conversely, it is in the tendency for the stabilized molded product whose surging phenomenon at the time of shaping increased to no longer be obtained. Especially concerning the method of blending above-mentioned (a) - (d) and also the above (e), (f), it is not limited but the arbitrary blend methods, such as the method

of pelletizing and drying with the method of carrying out a dry blend with a Banbury mixer etc., the extrusion machine of a monopodium or two axes, etc., may be adopted. The above-mentioned EVOH system resin composition (mixed material) is fabricated by the shape of a film, a sheet, a container, etc. by melt molding. As a melt molding method, arbitrary melt molding methods including an extrusion method (a blow molding method and an extrusion coating method are included) and injection molding process may be adopted.

[0024]It is preferred to set resin temperature as 235-260 **, and to carry out melt molding in this melt molding method, When gel, a fish eye, etc. occur in the extrusion molding of the long time [temperature / this] in less than 235 ** and 260 ** is exceeded conversely, foaming in a film, coloring of a film, the regurgitation instability at the time of shaping, etc. happen, and it is 240-250 ** desirable more preferably. The above-mentioned resin composition (layer) is laminated with various kinds of resin layers, and serves as a multilayer-structure object, and a various application is presented with it. The resin composition of this invention is especially arranged on an interlayer, Especially the multilayer-structure object acquired by carrying out multilayer co-extrusion molding as the multilayer-structure object and polyolefin system resin which are obtained by carrying out multilayer co-extrusion molding as polyamide system resin is arranged on both outer layers are arranged on both (passing adhering resin) outer layers is important, The latter of the former is useful to the wrapping for retorts as a material for damping of a gas tank, the hose for refrigerant gases, structural interior materials (wallpaper, flooring, etc.), etc. The above-mentioned wrapping for retorts is explained concretely.

[0025]As laminated constitution, although the resin composition layer / polyamide system resin layer of a polyamide system resin layer / this invention are mentioned like the above, If practicality, such as heat-sealing nature and gas barrier property under high humidity, is taken into consideration, (Inside) Laminated constitution, such as a resin composition layer / polyamide system resin layer of a thermoplastic resin layer / polyamide system resin layer / this invention (outside), a resin composition layer / polyamide system resin layer / thermoplastic resin layer

(outside) of a thermoplastic resin layer (inside) / polyamide system resin layer / this invention, is mentioned. The above-mentioned thermoplastics removes polyamide system resin. As polyamide system resin used for the above-mentioned polyamide system resin layer, Nylon 6, nylon 6 and 4, Nylon 66, nylon 6 and 9, Nylon 612, Nylon 11, Nylon 12, and these copolymers, Amorphous polyamide etc. are mentioned and especially the mixed material of nylon 6, nylon 6, the copolymer of Nylon 12 and nylon 6, and amorphous polyamide, etc. are useful.

[0026] As thermoplastics used for the above-mentioned thermoplastic resin layer, The publicly known thermoplastics for sealant (heat sealing) used for heat sealing of a resin made container, a bag, etc. can be used arbitrarily, The polypropylene which carried out the graft polymerization of a polypropylene homopolymer and the ethylene concretely, Use said polypropylene as a base and High density polyethylene, low density polyethylene, What blended straight-chain-shape low density polyethylene, an ethylene-vinylacetate copolymer, etc., Polyolefin system resin, such as high density polyethylene other than polypropylene, When copolyester etc. are mentioned and it takes into consideration that they are heat-sealing nature, transparency, and the retort field, a polypropylene homopolymer, Although what used as the base the polypropylene which carried out the graft polymerization of the ethylene, and said polypropylene, and blended high density polyethylene, low density polyethylene, straight-chain-shape low density polyethylene, an ethylene-vinylacetate copolymer, etc. is used especially suitably, When heat-sealing nature in particular is not needed, high density polyethylene, medium density polyethylene, low density polyethylene, vinyl acetate, acrylic ester or a butene, a hexene, The polyethylene which carried out copolymerization of the alpha olefins, such as 4-methyl-1-pentene, Ionomer resin, a polypropylene homopolymer, the polypropylene that carried out the graft copolymerization of the ethylene, Or the polypropylene which carried out copolymerization of the alpha olefins, such as ethylene, a hexene, and 4-methyl-1-pentene, Polyolefin system resin, such as poly-1-butene and poly-4-methyl-1-pentene, Polyvinyl chloride system resin, acrylic resin, polyvinylidene chloride system resin, Polyacetal system

resin, polyester system resin, polycarbonate system resin, Polystyrene system resin etc. are mentioned, these resin is independent or two or more sorts of mixed material are used, What used as the base a polypropylene homopolymer, the polypropylene which carried out the graft polymerization of the ethylene, and said polypropylene, and blended high density polyethylene, low density polyethylene, straight-chain-shape low density polyethylene, an ethylene-vinylacetate copolymer, etc. especially is used suitably.

[0027]In manufacture of the multilayer-structure object for retorts,As mentioned above, the co-extruding methods, such as the T-die method and a tubular film process, a blow molding method, Although publicly known methods, such as the co-injecting method, can be adopted and it is not limited in particular, the manufacturing method of the multilayer-structure object of the resin composition layer / polyamide system resin layer composition of above-mentioned polyamide system resin layer / this invention by the co-extruding method is explained below as an example of a manufacturing method.

[0028]When manufacturing the above-mentioned multilayer-structure object by the co-extruding method, after co-extruding from the set-up T die with a temperature of about 240-250 ** using the two-sort co-extrusion-molding device of three layers, it can cool with a chilled roll etc. and the layered product of three layers can be obtained. Although this method is laminated without using adhesive resin, Laminating via adhesive resin is also possible and as this adhesive resin Polypropylene, the monomer (vinyl acetate.) which can carry out copolymerization to polyethylene or ethylene The resin which the maleic anhydride etc. added polyolefin system resin, such as copolymers, such as acrylic ester, and denaturalized is used, By the three-sort co-extrusion-molding device of five layers of the resin composition layer / adhesive resin / polyamide system resin layer of a polyamide system resin layer / adhesive resin / this invention, the good multilayer-structure object of film appearance is acquired.

[0029]The multilayer-structure object like the above can also be acquired using a dry lamination process and extrusion lamination process etc. That is, the resin composition layer of this invention and each class of the

polyamide system resin layer are beforehand fabricated with the biaxial extrusion machine etc., and the method of carrying out dry laminate of this each class with adhesive resin, such as a urethane system, etc. are mentioned. The resin composition layer / polyamide system resin layer of above-mentioned thermoplastic resin layer / polyamide system resin layer / this invention, Also about multilayer-structure objects of four or more layers, such as a resin composition layer / polyamide system resin layer / thermoplastic resin layer of a thermoplastic resin layer / polyamide system resin layer / this invention, a multilayer-structure object is producible by the same method as the above.

[0030] Besides the multilayer-structure object illustrated with the above-mentioned multilayer co-extrusion molding, a dry lamination process and extrusion lamination process, etc., As lamination of the multilayer-structure object using the resin composition layer of this invention, If the resin composition layer of this invention is set to E and T and a polyamide system resin layer are set to P for a thermoplastic resin layer, Lamination, such as T/E/P, E/T/E/T, E/P/E/P, E/T/E/P, T/E/T/E/T, P/E/P/E/P, T/E/P/E/T, E/P/E/T, P/E/P/E/T, and P/E/T/E/T (all omit an adhesives layer), can be mentioned.

[0031] In this multilayer-structure object, as for the thickness of the resin composition layer of this invention, although the thickness of each class cannot generally be said according to the kind of layered product (multilayer-structure object), 3-250 micrometers is especially desirable still more preferred, and 5-80 micrometers is preferred at 5-100 micrometers. 3-500 micrometers is especially desirable still more preferred, and, as for the thickness of a polyamide system resin layer and a thermoplastic resin layer, 5-150 micrometers is preferred at 5-300 micrometers. This multilayer-structure object is useful as a film package material for retort sterilization processing, and lid material, pouches, a vacuum package, skin packaging, a deep-drawing package, and a rocket package are mentioned as a more concrete use of this film package material.

[0032] The method of heat sealing with a heat seal method is suitably used for the container which consists of thermoplastics, such as polypropylene in which this lid material laminated oxygen gas-barrier-property resin. This

lid material can be opened excelling in transparency and checking contents. These pouches are used with the gestalt of a three-way-type seal, a four-quarters seal, a pillow, a gazette, a standing pouch, etc.

[0033]The above-mentioned multilayer-structure object can demonstrate the characteristic which was excellent also as containers, such as a cup or a tray, in addition to the above-mentioned film packaging. After fabricating the sheet by co-extrusion molding and carrying out heat softening as a forming process of a container, Arbitrary methods, such as the method of fabricating in a predetermined container by vacuum forming method, plug-assist-forming method, pressure-forming method, the CD method, etc. and injection molding process, are used, and also it can also be made tube shape or the shape of a bottle by blow molding.

[0034]The container which uses this multilayer-structure object with the gestalt of lid material, a pouch, a tray, cups or a bottle, and a tube can carry out hot water heat-treatment publicly known as retort sterilization processing or voile germicidal treatment. As for retorting, various kinds of methods, such as a recovery type, a substitution type, a steamy type, a shower type, and a spray type, are adopted. When it uses for containers which consist of this multilayer-structure object, such as lid material, a pouch, a tray, cups or a bottle, and a tube, Retort sterilization processing can be performed in the state where it was filled up with foodstuffs, such as soup, miso soup with pork and vegetables, meat sauce, Japanese pot-au-feu, pilaf, Japanese noodles, sweet-and-sour pork, a hamburger, a steak, and cooked curry.

[0035]Next, the multilayer-structure object in the case of using the EVOH system resin composition of this invention as a material for damping of a gas tank, structural interior materials (wallpaper, flooring, etc.), etc. is explained. As composition of the multilayer-structure object used for this use, laminated constitution with the resin composition layer and polyolefin resin layer of this invention, a polyvinyl-chloride-resin layer, etc. is mentioned, As a gas-tank use, the resin composition layer/polyolefin resin layer of a polyolefin resin layer/this invention are used, and, specifically, the resin composition layer / polyvinyl-chloride-resin layer of a polyvinyl-chloride-resin layer / this invention are suitably used as a structural interior material (wallpaper, flooring, etc.) use.

[0036]As polyolefin system resin used for the above-mentioned multilayer-structure object, Polypropylene, high density polyethylene, low density polyethylene, linear low density polyethylene, Ethylene-vinylacetate copolymers or these copolymers, a denaturation thing, etc. are mentioned, and polypropylene, high density polyethylene, low density polyethylene, and linear low density polyethylene are used suitably especially. In manufacture of this multilayer-structure object for damping, it can manufacture by the same method as the film package material for the above-mentioned retort sterilization processing. As mentioned above, although the gas tank of the film package material for retort sterilization processing or a damping nature use and structural interior materials (wallpaper, flooring, etc.) were explained as a multilayer-structure object using the EVOH system resin composition of this invention, uses, such as a blow bottle and a hose for refrigerant gases, can be presented besides these.

[0037]

[work --] for The EVOH system resin composition of this invention, without reducing the characteristic which EVOH (s), such as gas barrier property, oil resistance, and solvent resistance, have, Are useful on multilayer-structure objects for which it excels in a long-run moldability, the Takanobu extensibility with an area magnification of 20 or more times, etc., and the film package material for retort sterilization processing and damping nature are especially needed, such as a gas tank, a structural interior material, and a hose for refrigerant gases, In manufacturing this multilayer layered product, the effect of a prolonged processing moldability also does so by carrying out extrusion molding of the gas-barrier-property resin layer which consists of an EVOH system resin composition at 235-260 **.

[0038]

[Example]Hereafter, an example is given and this invention is explained still more concretely. The following (a) - (d) and (e), and (f) were prepared.

EVOH(a)a-1:degree % and MI (melt index) =3.0(210 **, 2160g load)a-2: Degree % of 99.6 mol of ethylene content % and saponification of 27 mol, MI=8.0 (same as the above) [of ethylene content % and saponification of 32 mol] [of 99.5 mol]

a-3: Degree % of 99.8 mol of ethylene content % and

saponification of 29 mol, MI=8.0 (same as the above)
EVOH(b) b-1:degree % and MI =12.0(same as the above)b-
 2: Degree % of 99.6 mol of ethylene content % and
 saponification of 47 mol, MI=5.4 (same as the above) [of
 ethylene content % and saponification of 44 mol] [of 99.5
 mol]
 b-3: Degree % of 98.5 mol of ethylene content % and
 saponification of 38 mol, MI=3.0 (same as the above)
 b-4: Degree % of 91.5 mol of ethylene content % and
 saponification of 44 mol, MI=3.0 (same as the above)
 [0039]End adjustment polyamide system resin (c) c-1 :
 Nylon 612 (weight ratios 90/10) is made into an end
 modifier. thing terminal carboxyl group content [X] which
 carried out end regulation by ***** -- 38microeq/g
 terminal amino group content [Y] ratio [of the number of
 22microeq/g methylene groups to the number of amide
 groups] (CH_2/NHCO): -- 5.35 melting point; -- 211 **
 [0040]c-2: Nylon 612 (weight ratios 80/20) is made into an
 end modifier. thing terminal carboxyl group content [X]
 which carried out end regulation with ** stearic acid --
 47microeq/g terminal amino group content [Y] ratio [of the
 number of 17microeq/g methylene groups to the number of
 amide groups] (CH_2/NHCO): -- 5.70 melting point; -- 195
 **[0041]c-3: The nylon 6 66 and 12 (weight ratio 75/15/10)
 is made into an end modifier. thing terminal carboxyl group
 content [X] which carried out end regulation by *****
 -- 45microeq/g terminal amino group content [Y] ratio [of
 the number of 38microeq/g methylene groups to the number
 of amide groups] (CH_2/NHCO): -- 5.38 melting point; --
 178 ** [0042]Aliphatic-carboxylic-acid alkaline earth metal
salt.(d) d -1:magnesium acetate 4 hydrate d-2:calcium
 propionate d-3: -- butanoic acid magnesium hindered phenol
system compound (e) e-1:N,N'-hexa methylenebis (3,5-di-t-
 butyl-4-hydroxyhydronalium SHINNAMIDO)
 ("IRUGA NOx 1098" by a tiba guy key company)
 e-2: 1,3,5-trimethyl 2,4,6-tris(3,5-di-t-butyl-4-
 hydroxybenzyl) benzene ("IRUGA NOx 1330" by a tiba guy
 key company)
 e-3: Pentaerythrityl tetrakis [3-(3,5-di-t-butyl-4-
 hydroxyphenyl) propionate]
 ("IRUGA NOx 1010" by a tiba guy key company)
 [0043]Lubricant (f) f-1:ethylene screw stearyl AMAIDO f-

2: Polyethylene (the molecular weight 3200 by a viscosity method, acid value 20 KOHmg/g)

f-3: Zinc stearate f-4 : magnesium stearate f-5:zinc stearate / calcium stearate =1/0.5 (weight ratio)

[0044]It cooled after melt kneading with the twin screw extruder (or single screw extruder), and (a) - (d) ingredient (adding (e) and the (f) ingredient further) shown in Examples 1-11 and the comparative example 1-11 <monolayer melt molding> tables 1-6 was pelletized. Subsequently, melting extrusion of this pellet was supplied and carried out to the extrusion machine provided with the T die, and 100-micrometer-thick monolayer film (I) was produced. Extrusion-molding conditions were set up as follows.

extrusion machine: -- diameter extruder screw [of 40 mm]:
-- full flight die pressing appearance temperature: -- the extrusion machine temperature of 230 **, the die temperature of 250 **, and resin temperature 245 ** screw-speed:40rpm [0045]Although the gas barrier property of monolayer film (I) obtained in Example 1, oil resistance, and solvent resistance were evaluated as the following, all are convenient practical [what is accepted compared with an EVOH (a-1) simple substance as for some falls].

(Gas barrier property) With OXTRAN10 / 50 type (made by MOCON) measuring instrument, the measured oxygen transmittance of above monolayer film (I) and an EVOH (a-1) film, It was 2.3 (cc, 20 micrometer/m², and day-atm) and 0.6 (cc, 20 micrometer/m², and day-atm), respectively. (Oil resistance) Although above monolayer film (I) was immersed in gasoline, gas oil, kerosene, and a fuel oil for seven days at the room temperature, a remarkable appearance change was not accepted like the EVOH (a-1) film.

[0046](Solvent resistance) Although above monolayer film (I) was immersed in benzene, toluene, acetone, and a carbon tetrachloride for seven days at the room temperature, a remarkable appearance change was not accepted like the EVOH (a-1) film.

<Co-extrusion molding> (a) - (d) shown in Tables 1-6 like 90 % of the weight of nylon 6 resin, the polyamide system resin Y containing 10 % of the weight of amorphous polyamide, and the above, (a) It co-extruded so that it might become the lamination of Y/X/Y from the T die which set

the resin composition X which consists of - (e) and (a) - (f) as the temperature of 245 **. Then, heat setting was carried out in the atmosphere in 210 **, extending 3 times with a 90 ** roll drawing machine, and also making it about 4% of width extension and reduce by the tenter continuously 3.5 times with the tenter drawing machine of 100 ** atmosphere. The class thickness of obtained multilayer-structure object (II) was Y/X/Y=5/10/5 (micrometer). The following evaluations were performed about monolayer film (I) and multilayer-structure object (II) which were obtained above.

[0047](Orientation processability) A 10x10-cm film (20 sheets) was extracted from monolayer film (I) five days after being obtained by performing the above-mentioned <monolayer melt molding> continuously for five days, simultaneous biaxial stretching (5x5 times) was performed on condition of the following (20 times), and the number of sheets of the success film at that time was counted. That carries out visual observation of the appearance of the film after biaxial-stretching processing, and troubles, such as a fracture and a hole vacancy, are not accepted to be to a film was used as the success film.

Biaxial-stretching machine: Made in Iwamoto Factory, extension temperature:100 ** stretching speed:100m/sec

[0048](Retort nature) After performing retort sterilization processing for multilayer-structure object (II) obtained above for 30 minutes in a 121 ** steam atmosphere using a retort device (the Yamato Scientific Co., Ltd. make, autoclave SM-31), visual observation of the appearance of multilayer-structure object (II) after neglect was carried out for room temperature 30 minutes. It gets with following one and a judging standard is **.

O --- It was transparent and discoloration was not accepted.

x --- Hayes or a white blush mark was accepted.

(Damping nature) tandelta (height, a position, half peak width) of the above-mentioned monolayer film (I) and multilayer-structure object (II) was measured on condition of the following using the DVE-V4 LEO spectra Made from Rheology.

temperature: -100-200 ** heating-rate: -- 3 ** / min

frequency: -- 10-Hz sample size: -- 20x5-mm gage length: --

10 mm -- gage thickness -- : -- 30 micrometers [0049]in

addition -- making the height of tandelta of monolayer film

(I), a position, and half peak width into damping nature (A.I. Artificial Intelligence), damping nature (BI), and damping nature (CI) in Tables 1-6, respectively -- the same -- each of multilayer-structure object (II) -- as damping nature (AII), damping nature (BII), and damping nature (CII) -- a table -- the bottom. The evaluation result of an example and a comparative example is combined with Tables 1-6, and is shown. The numerical value after the metal name of the (d) ingredient shown in Tables 1-6 expresses the loadings (mumol/g) of the metal to the total quantity of (a+b+c), and the number of (e) and the (f) ingredient expresses each blending ratio to the total quantity of (a+b+c) with a ppm value.

[0050]

[Table 1]

the example 1 example 2 example 3 example 4 (a) ingredient .a-1 49 copies a-1 68 copies a-1. Copies [49] a-2 49-Copy (B) Ingredient B-1. Copies [21] B-2 17 Copies B-1 21 Copies . b-1 21-copy (c) ingredient c-1 30 copies . c-1 15 copies c-2 30 copies c-1. 30-copy (d) ingredient d-1 Mg 2.0. d-1 Mg 2.3 d-3 Mg 1.5. d-2 Ca 2.1 (e) ingredient e-1. 4000ppm e-3 4000 ppm. - e-2 4000 ppm (f) ingredient . - - f-1 5000ppm orientation processability . 20 sheets 20 sheets 20 sheets 20 sheets Retort-proof nature O. O O O damping nature (A.I. Artificial Intelligence) 0.32 0.31. 0.33 0.33 -- damping nature (BI) 50 53 51 50 -- damping nature (CI) 90 80 91 90 damping nature (AII) -- 0.34 0.30 0.33 0.34 damping nature (BII) -- 48 51 50 49 damping nature (CII) -- 91 81 92 92[0051]

[Table 2]

the example 5 example 6 example 7 example 8 (a) ingredient . a-3 68 copies a-1 20 copies a-2. Copies [28] a-3 20-Copy (B) Ingredient B-3. Copies [17] B-3 30 Copies B-3 42 Copies . b-2 30-copy (c) ingredient c-2 15 copies . c-2 50 copies c-1 30 copies c-2. 50-copy (d) ingredient d-2 Mg 2.3. d-1 Mg 2.0 d-1 Mg 2.3. d-1 Mg 2.0 (e) ingredient e-1. 500ppm e-1 4000ppm e-3. 4000ppm e-3 4000 ppm (f) ingredient . f-2 5000ppm f-3 500 ppm. f-4 1000ppm f-5 1500ppm orientation processability . 20 sheets 20 sheets 20 sheets 20 sheets Retort-proof nature . O O O O damping nature (A.I. Artificial Intelligence) 0.30. 0.41 0.33 0.33 -- damping nature (BI). 51 45 50 44 -- damping nature (CI) 80 110 91 110 damping nature (AII) -- 0.32 0.42 0.34 0.42

damping nature (BII) -- 50 46 50 46 damping nature (CII) -- 82 112 94 110[0052]

[Table 3]

the example 9 example 10 example 11 (a) ingredient . a-3 68 copies a-3 20 copies a-3. 28-copy (b) ingredient b-4 17 copies b-4. Copies [30] B-4 42-Copy (C) Ingredient C-2. Copies [15] C-2 50 Copies C-1 30-Copy (D) Ingredient . d-2 Mg 2.3 d-1 Mg 2.0. d-1 Mg 2.3 (e) ingredient e-1. 1000ppm e-1 4000 ppm. e-3 4000 ppm (f) ingredient f-2. 5000ppm f-3 1000 ppm. f-4 1000ppm orientation processability 20 sheets . 20 sheets Retort-proof [20-sheet] nature O O O damping nature (A.I. Artificial Intelligence). 0.31 0.41 0.34 damping nature (BI) 50 44 48 damping nature (CI) 82 115 90 damping nature (AII) -- 0.33 0.41 0.36 damping nature (BII) -- 49 46 47 damping nature (CII) -- 84 116 95[0053]

[Table 4]

the comparative example 1 comparative-example 2 comparative-example 3 comparative-example 4 (a) ingredient . a-1 70 copies a-1 70 copies a-1. Copies [49] a-1 69-Copy (B) Ingredient - B-1. Copies [30] B-1 21 Copies B-1 29 Copies . (c) Ingredient c-1 30 copies - c-1. Copies [30] C-1 Two-Copy (D) Ingredient D-1. Mg 2.0 d-1 Mg 2.0 -. d-1 Mg 2.0 orientation processability Three sheets Zero sheet . zero sheet Zero sheet Retort-proof nature O O O O damping nature (A.I. Artificial Intelligence). 0.38 0.15 0.330.16 -- damping nature (BI). 61 80 50 80 -- damping nature (CI) 70 20 90 21 damping nature (AII) -- 0.39 0.16 0.34 0.17 damping nature (BII) -- 50 80 50 80 damping nature (CII) -- 70 21 92 20[0054]

[Table 5]

the comparative example 5 comparative-example 6 comparative-example 7 comparative-example 8 (a) ingredient . a-1 47 copies a-1 49 copies a-1. Copies [49] a-1 49-Copy (B) Ingredient B-1. Copies [23] B-1 21 Copies B-1 21 Copies . b-1 21-copy (c) ingredient c-1 60 copies . c-1 30 copies c-1 30 copies c-1. 30-copy (d) ingredient d-1 Mg 2.0. d-1 Mg 18 d-1 Mg 0.3. d' Na 3.0 orientation processability Ten sheets -. zero sheet Retort-proof [zero-sheet] nature O - - - damping nature (A.I. Artificial Intelligence). 0.30 - - - damping nature (BI) 48 - - - damping nature (CI) 60 - - - damping nature (AII) -- 0.32 - - - damping nature (BII) -- 49 - - - damping nature (CII) -- 60 -

-- notes d' -- sodium acetate The comparative example 6, Foaming arises at the time of monolayer film shaping, and a satisfactory film is not obtained. Orientation processability, retort-proof nature, and damping nature are not evaluated. a satisfactory multilayer-structure object acquires the comparative examples 7 and 8 for a poor moldability (gel abundant generating) ** -- **** -- retort-proof nature and damping nature are not evaluated.

[0055]

[Table 6]

the comparative example 9 comparative-example 10 comparative-example 11 (a) ingredient . a-1 49 copies a-1 95 copies a-1. Copies [Five] (B) Ingredient B-1 21 Copies B-1. Copies [Five] B-195 Copies (C) Ingredient C-1. Copies [30] C-1 30 Copies C-1 30-Copy (D) Ingredient . d-3 Mg 2.0 d-1 Mg 2.0. d-1 Mg 2.0 orientation processability Zero sheet Seven sheets . retort-proof [11 sheet] nature - O O damping nature (A.I. Artificial Intelligence). - 0.28 0.30 damping nature (BI) - 58 55 damping nature (CI) - 69 70 damping nature (AII) - 0.29 0.31 damping nature (BII) - 59 56 damping nature (CII) - 71 71 notes comparative example 9, A satisfactory multilayer-structure object is acquired for a poor moldability (gel abundant generating). **, retort-proof nature, and damping nature are not evaluated.

[0056]The heat sealer performed heat adhesion to the cup like container made from polypropylene into which water went by making into lid material multilayer-structure object (II) obtained in example 12 Examples 1-11 by using unextended polypropylene layers as an inner surface. 121 ** and retort sterilization processing for 30 minutes were performed using the retort device in which this was shown according to an above-mentioned example and comparative example. Immediately after retorting, the film of the lid was transparent, it did not have a wave pattern etc. and its appearance was good.

[0057]Heat-sealing processing of multilayer-structure object (II) obtained in example 13 Examples 1-11 was carried out at the shape of a pouch, water was put into inside, and the regio oralis was heat sealed. 121 ** and retort sterilization processing for 30 minutes were performed using the retort device in which this was shown according to an above-mentioned example and comparative example. Immediately after retorting, the pouch was transparent, it did not have a

wave pattern etc. and its appearance was good.

[0058]Example 14 high-density-polyethylene resin / adhesive resin. The resin composition / adhesive resin (carboxylic acid modified polyethylene system resin) / high-density-polyethylene resin of this invention of (carboxylic acid modified polyethylene system resin) / Example 1 = The 5x5x5-cm Multi-layer bottle which consists of 300 micrometers/50 micrometer/50 micrometer/50 micrometer/300 micrometer (thickness). It fabricates (the inlet of gasoline is provided and it enabled it to seal with the cap made from polyethylene), After attaching this bottle to the Shimazu omnipotent fatigue testing machine and adding 10^6 time cyclic fatigue by the amplitude of 1 mm, and 1 kg of load, about 100 ml of gasoline was put into this bottle, and it sealed with the cap. This sealing bottle was neglected for one week by the sealed state in glassware (desiccator), the gas in this glassware was extracted, and gas chromatography analyzed the gasoline component.

Although gasoline was put into the bottle which is not got fatigued for comparison and the gasoline component was measured similarly, both were not permitted the difference, but the Multi-layer bottle using the resin composition of this invention showed the good result also in the gas-tank use. Although the evaluation same also about monolayer film (I) of Examples 2-11 as the above was performed, the good result was obtained like [in any case] the above.

[0059]After carrying out the extrusion lamination of the resin composition used for a PVC (polyvinyl chloride) film with an example 15 thickness of 1 mm at monolayer film (I) of Example 1 so that it may become a thickness of 10 micrometers, and obtaining a laminated film, BURUYU -- a well -- the loss coefficient of this laminated film was evaluated using & care (B&K) damping-performances automatic measuring system. The big peak appeared near the room temperature and the result checked that a damping characteristic was good. Although the evaluation same also about monolayer film (I) of Examples 2-11 as the above was performed, the good result was obtained like [in any case] the above.

[0060]

[Effect of the Invention]The EVOH system resin composition of this invention, without reducing the characteristic which EVOH(s), such as gas barrier property,

oil resistance, and solvent resistance, have, Are useful on multilayer-structure objects for which it excels in a long-run moldability, the Takanobu extensibility with an area magnification of 20 or more times, etc., and the film package material for retort sterilization processing and damping nature are especially needed, such as a gas tank and a structural interior material, In manufacturing this multilayer-structure object, the effect of a prolonged processing moldability also does so by carrying out extrusion molding of the gas-barrier-property resin layer which consists of an EVOH system resin composition at 235-260 **.

[Translation done.]